

VII.16 Sorbents for the Removal of Odorants from Natural Gas

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Objectives

- Identify the sorbent composition that maximizes the sorbent's capacity for organosulfur compounds
- Identify the sorbent's pre-breakthrough absorption and saturation capacity for organosulfur compounds
- Identify optimum operating conditions (i.e. temperature, pressure, contact time)
- Identify the effect of other natural gas contaminants such as CO₂, humidity and heavier hydrocarbons on sorbent performance

Approach

- Develop two types of sorbents: a high-temperature chemical sorbent and a low-temperature physical sorbent
- Screen the sorbents to rank their ability to remove odorants from simulated natural gas and liquefied petroleum gas (LPG)
- Optimize the conditions and demonstrate the effects of potential natural gas and LPG impurities on sorbent performance

Accomplishments

- Two types of sorbents were developed: a high-temperature chemical sorbent with an optimum operating temperature of 240°C and an ambient-temperature physical sorbent
- Both sorbents can reduce the sulfur content to less than 20 ppbv, achieving greater than 99.99% sulfur removal efficiency
- Both sorbents can remove all common organic sulfur species as well as H₂S
- Neither sorbent catalyzes any undesirable side reactions
- The absorption capacity for removing dimethyl sulfide from natural gas is 5.51% for the chemical sorbent and 2.52% for the physical sorbents
- For LPG, the chemical sorbent has a 0.47% wt. sulfur absorption capacity while the physical sorbent has 1.23% wt. sulfur adsorption capacity
- We showed that our ambient-temperature physical sorbent can also be regenerated by applying a mild temperature swing

Future Directions

- Develop a fundamental understanding of the removal process and the nature of the active sites so that we can optimize and improve the sorbent formulations
- Carry out long-duration tests where the regeneration potential of the physical adsorbent is demonstrated over multiple adsorption/regeneration cycles

- Carry out field tests to demonstrate the performance of our desulfurization sorbents integrated with a fuel cell system (with fuel cell stacks, fuel processor and all auxiliary items)
- Carry out an independent engineering study to assess the impact of TDA's novel desulfurization technologies on overall system efficiency, weight and cost

Introduction

Chemical odorants made with sulfur-containing compounds are added to natural gas and liquefied petroleum gas (LPG) to facilitate leak detection. However, these compounds contaminate the catalysts used in fuel cell fuel processing systems and degrade the performance of the fuel cell stacks.

We developed low-cost, high-capacity sorbents that can remove sulfur-bearing odorants from natural gas and LPG. We also demonstrated the technical and economic feasibility of processes using these sorbents, which dramatically reduce the cost of odorant removal.

Approach

The overall objective of the Phase I research was to determine the technical and economic feasibility of using a sorbent to remove sulfur-bearing odorants from natural gas and liquefied petroleum fractions such as propane. To accomplish this objective, we developed two different types of sorbents: a low-temperature physical adsorbent and a high-temperature chemical absorbent.

To prepare both types of sorbents, we first identified several precursors for the active phase and substrate matrix. A large number of these preparations (both physical and chemical sorbents) were first pre-screened based upon their physical properties (i.e., crush strength, surface area, porosity). Only the best samples were tested in the bench-scale reactor to determine their sulfur absorption capacity.

We built a testing system and developed an analytical method to allow us to measure the performance of both types of sorbents (high- and low-temperature) with a sulfur detection capability of 20 ppbv. We screened over 40 samples and identified the samples with the highest sulfur absorption capacity under representative conditions (using natural gas blends and LPG). We tested the

effect of different operating parameters on the sulfur absorption capacity of the sorbents and showed that we can develop sorbents with a very high sulfur absorption capacity. We showed the effectiveness of the sorbents for removing different odorant species, including dimethyl sulfide (DMS), tetrahydrothiophene (THT), tert-butyl mercaptan (TBM), and isopropyl mercaptan (IPM) at representative concentrations from natural gas and LPG blends. In all cases, dimethyl sulfide was found to be the hardest odorant to remove.

Results

In our research, we first recognized that a chemically active sorbent that works at high temperatures (240°C) could effectively remove more sulfur-bearing odorants from natural gas than a room-temperature sorbent. We developed a very active chemical absorbent that effectively removes even the most difficult to react organic sulfur species (such as dimethyl sulfide). Figure 1 shows the breakthrough profiles for a test done with multiple odorants. As the test starts, there are no odorants present in the exit gas stream, as they are all absorbed by the sorbent. During absorption, the sorbent forms a stable sulfide phase while reducing sulfur content of the natural gas to less than 20 ppbv (the detection limit of our Phase I apparatus). The DMS then

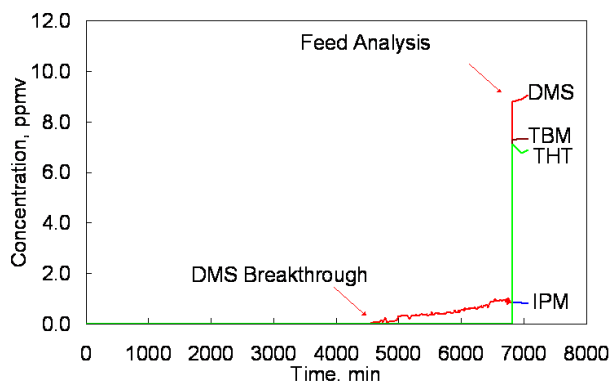


Figure 1. Adsorption Profile for the High-Temperature Sorbent Using a Mix of Odorants

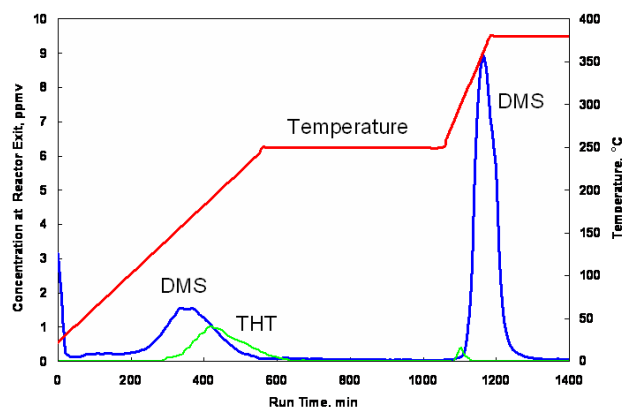


Figure 2. Regeneration of a Low-Temperature Physical Sorbent

breaks through. After the test was finished, the inlet gas stream was run through the analyzers to show that all of the sulfur compounds were present still in the correct proportions in the feed. The chemical absorbent we developed in the Phase I work achieves 5.51% wt. absorption capacity (lb of sulfur removed per lb of sorbent), nearly an order of magnitude higher than can be achieved by conventional sorbents. We also demonstrated that the operating temperature of the sorbent does not catalyze any undesirable side reactions (e.g., oxidation of natural gas or reactions among the organic sulfur species).

Based on the feedback from the fuel cell manufacturers, we also developed an ambient-temperature adsorbent that removes the odorants by physical adsorption. TDA's physical adsorbent achieved 2.52% wt. sulfur adsorption capacity, a great improvement in capacity over state-of-the-art room-temperature adsorbents (the best result reported in the literature to date is ~1.2% wt. by King and coworkers using copper and cerium exchanged zeolites). TDA's physical adsorbent was also very effective in removing organic sulfur compounds from LPG. We showed that our ambient-temperature sorbent can be regenerated by applying a mild temperature swing. Figure 2 shows a profile of a regeneration cycle. The sample was originally tested in a mixture of 17 ppmv DMS, 5 ppmv THT, 7 ppmv TBM. After testing, the sample was regenerated in

nitrogen. As the temperature was raised, the off-gas was monitored for sulfur compounds. The figure shows that at 150°C, some DMS and THT were released, and at 350°C, more DMS was released.

Conclusions

In our research, we developed very effective sorbents for desulfurization of natural gas and LPG. We first developed a very active chemical absorbent and showed that the sorbent forms a stable sulfide phase. The sorbent achieves 5.51% wt. sulfur absorption capacity for removing dimethyl sulfide from natural gas and can desulfurize LPG with 0.47% wt. sulfur absorption capacity.

We also developed a low-temperature adsorbent that removes the odorants by physical adsorption. The sorbent achieves 2.52% wt. sulfur adsorption capacity for removing dimethyl sulfide from natural gas and can desulfurize LPG with 1.23% wt. sulfur adsorption capacity. We showed that our ambient-temperature sorbent can be regenerated by applying a mild temperature swing.

References

1. King, D.L., Birnbaum, J.C., Singh, P., "Sulfur Removal from Pipe Line Natural Gas Fuel: Application to Fuel Cell Power Generation Systems", Proceedings of the 2002 Fuel Cell Seminar, Palm Springs, CA.

FY 2004 Publications/Presentations

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2. Alptekin, G.O., Amalfitano, B., Copeland, R., "Sorbents for Natural Gas Clean-up", Fuel Cell Seminar, Miami Beach, FL, 2003.